Effects Of The Endgroup On The Growth And The Order Of CH_3- And CF_3-Terminated Alkanethiols

J. Pflaum, G. Scoles, A. Kahn (Princeton U.), G. Bracco (U. of Genova, Italy), F. Schreiber (MPI für Metallforschung, Germany), R. Colorado, and R. Lee (U. of Houston)

Abstract No. Pfla1628
Beamline(s): **X10B**

Introduction: Self-assembled monolayers (SAMs) of alkanethiols are ideally suited as interlinks between a given substrate and an organic thin film, because of their long-range lateral order [1]. By tailoring their chemical composition thiols can form active interfaces with defined mechanical properties, e.g. friction force, and electronic properties, e.g. transport gap [2, 3]. However, engineering of the thiols' functionality, e.g. by changing their endgroup, also affects the growth phases, the lateral coherence, and the thermal stability of those films. For these reasons studies of the interplay between the functionalization and the growth of thiols are of great importance.

Methods and Materials: In this project we compare alkanethiols with CF_3- and CH_3-termination. The experiments are performed at beamline X10B using grazing incidence x-ray diffraction (GIXD) and reflectivity measurements. The thiol films were prepared on Au(111) single crystals by vapor deposition in UHV and from solution. All measurements were carried out in UHV at a base pressure of about $4 \cdot 10^{-9}$ Torr. Using STM and He-Scattering complementary data on the surface properties of the SAMs were obtained.

Results: On CH_3-terminated thiol films GIXD clearly shows a well-defined lateral ordering of the molecules with a hexagonal rotational symmetry induced by the underlying Au substrate. In addition, the well-known c(4x2) superstructure is found. From rodscans and comparisons of the nominal thicknesses with thicknesses calculated from structural models it has been found that at full coverage the thiols form a standing up phase at a tilt angle of about 30^o with respect to the surface normal. In contrast, for thiols with substituted endgroup ($CH_3 \rightarrow CF_3$) no in plane diffraction peaks are found, neither for the hexagonal ($\sqrt{3}$x$\sqrt{3}$) lattice nor for the c(4x2) superstructure. He-scattering and STM data support the notion that no long-range order of the fluor-terminated thiols occurs at RT (at low temperatures He-scattering has detected the presence of lateral ordering). Nevertheless, as shown in **Figure 1** for two ω-fluorinated thiols of different chain lengths modulation in the reflectivity curves can be observed. The nominal thickness deduced from the curves clearly indicates that the layers are built by thiols standing upright on the Au substrate. With respect to the structural data, the fluor-terminated thiol layers show a rather liquid like behavior at room temperature (RT). The observed behavior is likely to be related to the larger van-der-Waals radius for the CF_3-endgroup compared to the CH_3-termination. Moreover, the higher charge density in the case of CF_3 may cause a larger electrostatic repulsion between the molecules and, therefore, adds additional constraints to the formation of an ordered phase.

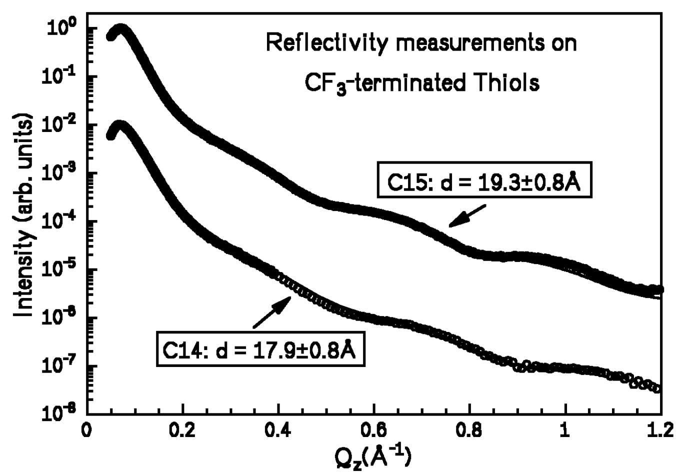

Figure 1. Reflectivity curves for CF_3-terminated C14 and C15.

Conclusions: GIXD measurements on CH_3- and on CF_3-terminated thiol monolayers show a significant influence of the endgroup on the morphology of these films. Whereas thiols with a CH_3-endgroup form domains of long-range order, for the CF_3-terminated alkanethiols no ordered phase can be observed at RT. As the voltage-current curves for CF_3-terminated thiols indicate a gap, making these systems interesting for controlled charge injection, studies on the growth of organic/organic heterostructures using CH_3- and CF_3-terminated thiols as building blocks are in progress [3, 4].

Acknowledgments: We thank S. Bennett and R. Kolb for collaboration. J.P. acknowledges the DFG (Grant No. PF 385/1-1) for their support.

References: [1] F. Schreiber, Prog. Surf. Sci., in print; [2] H.I. Kim, M. Graupe, O. Oloba, Th. Koini, S. Imaduddin, T.R. Lee, S.S. Perry, Langmuir **15**, 3179 (1999); [3] J. Pflaum, G. Bracco, F. Schreiber, R. Colorado, T.R. Lee, G. Scoles, A. Kahn, in prep.; [4] M.C. Gerstenberg, F. Schreiber, T.Y.B. Leung, G. Bracco, S.R. Forrest, G. Scoles, Phys. Rev. B **61**, 7678 (2000)